

Flammability and Thermal Stability Studies of Polymer Layered-Silicate (Clay) Nanocomposites - II

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ABSTRACT

In many of the cases studied, polymer-clay nanocomposites are materials that have improved thermal properties. Furthermore, most of the nanocomposite systems reported so far show reduced flammability. The delaminated versions of nanocomposites also offer measurable improvements in a variety of physical properties. The intercalated versions offer the above benefits, but with less improvement in physical properties. Many issues are unresolved as to the mechanism of these property enhancements. We report here on our continuing study of the mechanism of flammability reduction with recent results for polypropylene and polystyrene layered-silicate nanocomposites using montmorillonite and fluorohectorite.

INTRODUCTION

Nanocomposites. Polymer-clay nanocomposites were first reported in the literature as early as 1961, when Blumstein demonstrated polymerization of vinyl monomers intercalated into montmorillonite clay (1). The most recent methods to prepare polymer-clay nanocomposites have primarily been developed by several groups. In general these methods (shown in Figure 1) achieve molecular-level incorporation of the layered silicate (e.g., montmorillonite, or synthetic layered-silicate) into the polymer by addition of a modified silicate either during the polymerization (*in situ method*) (2, 3, 4) or to a solvent-swollen polymer (5), or to the polymer melt (6, 7). Additionally, a method has been developed to prepare the layered-silicate by polymerizing silicate precursors in the presence of a polymer (8).

Two terms (*intercalated* and *delaminated*) are used to describe the two general classes of nanomorphology that can be prepared. *Intercalated* structures are well ordered multi-layered structures where the extended polymer chains are inserted into the gallery space between the

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individual silicate layers (see Figure 2). The *delaminated* (or *exfoliated*) structures result when the individual silicate layers are no longer close enough to interact with the adjacent layers' gallery cations (9). In the *delaminated* cases the interlayer spacing can be on the order of the radius of gyration of the polymer; therefore, the silicate layers may be considered well dispersed in the organic polymer. The silicate layers in a *delaminated* structure may not be as well ordered as in an *intercalated* structure. X-ray diffraction measurements are used to characterize the nanostructures. Reflections in the low angle region indicate the d-spacing (basal spacing) of ordered intercalated and ordered delaminated nanocomposites; disordered nanocomposites show no peaks in this region due to the loss of structural registry of the layers and (or) the large d-spacings (> 10 nm).

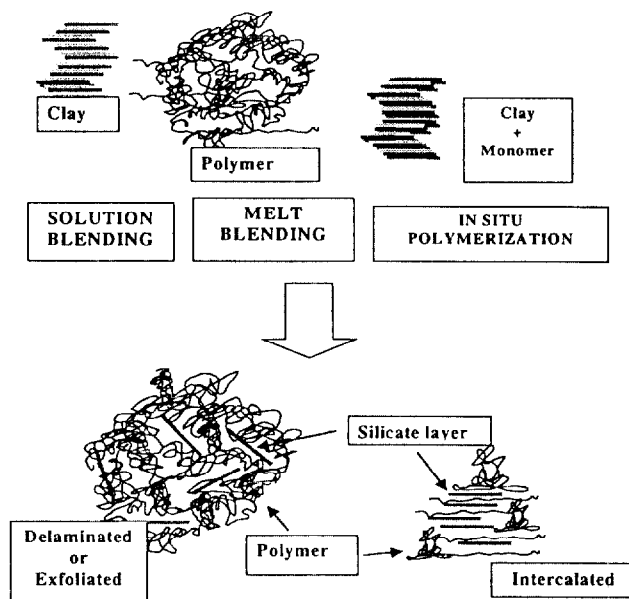


Figure 1. Schematic representation of various methods (solution blending, melt blending, and *in situ* polymerization) used to prepare polymer layered-silicate nanocomposites. The delaminated (or exfoliated) and intercalated morphologies are also shown.

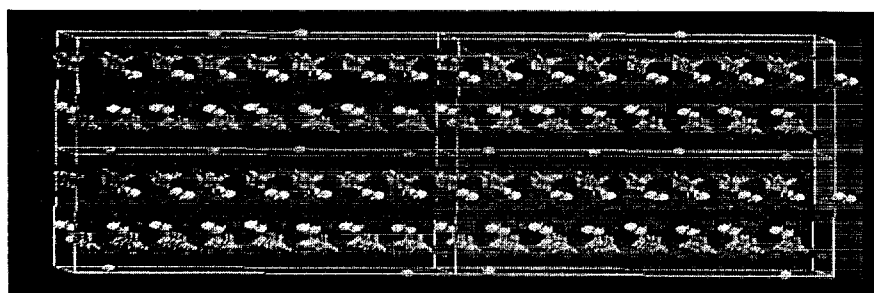


Figure 2. Molecular representation of sodium montmorillonite, showing two aluminosilicate layers with the Na^+ cations in the interlayer gap or gallery.

Polymer-clay nanocomposites have unique properties when compared to conventional filled polymers (6). For example, the mechanical properties of a nylon-6 layered-silicate

nanocomposite, with a silicate mass fraction of only 5 %, show excellent improvement over those for the pure nylon-6. The nanocomposite exhibits a 40 % higher tensile strength, 68 % greater tensile modulus, 60 % higher flexural strength, and a 126 % increased flexural modulus. The heat distortion temperature (HDT) is increased from 65 °C to 152 °C, and the impact strengths are only lowered by 10 % (10). The mechanical properties of aliphatic amine cured epoxy layered-silicate nanocomposites, reported recently by Pinnavaia, reveal a factor of 4 or more improvement in tensile modulus and tensile strength, and substantial *increase* in the strain-at-break (11). Decreased gas permeability, and increased solvent resistance also accompany the improved physical properties (6). Finally, as will be discussed below, polymer-clay nanocomposites often exhibit increased thermal stability (12, 13): an important property for high temperature applications and reduced flammability (14, 15, 16).

Thermal Stability. Blumstein (17) first reported the improved thermal stability of a polymer-clay nanocomposite that combined polymethylmethacrylate (PMMA) and montmorillonite clay. Although this clay-rich nanocomposite (mass fraction ~10 % *intercalated* PMMA) undoubtedly exhibits mechanical properties dominated by the inorganic phase, the indications of enhanced polymer thermal properties are clear. Blumstein showed that PMMA inserted between the lamellae of montmorillonite clay resisted thermal degradation under conditions that would otherwise completely degrade pure PMMA (refluxing decane, 215 °C, N₂, 48 h). These PMMA nanocomposites were prepared by free radical polymerization of methyl methacrylate (MMA) intercalated in the clay. X-ray analysis showed an increase of 0.76 nm in the basal spacing. Thermogravimetric analysis (TGA) reveals that both linear PMMA and crosslinked PMMA intercalated into Na montmorillonite have a 40 °C to 50 °C higher decomposition temperature. Blumstein argues that the stability of the PMMA-nanocomposite is due not only to its different structure, but also to restricted thermal motion of the PMMA in the gallery.

The first mention of the potential flame retardant properties of these type of materials appears in a 1976 Unitika patent application on nylon-6 clay nanocomposites (18). However, not until more recent studies of improved thermal stability were reported by Giannelis (12) did the serious evaluation of the flammability properties of these materials begin.

Giannelis found an improvement in thermal stability similar to that reported by Blumstein for both PDMS and polyimide nanocomposites. In this case (PDMS) the nanocomposite was not prepared by *in situ* polymerization in sodium montmorillonite, but by melt intercalation of silanol-terminated PDMS with dimethyl ditallow ammonium treated montmorillonite. In contrast to Blumstein's materials, this nanocomposite contained *primarily* PDMS (mass fraction 90 %) and only a 10 % mass fraction of montmorillonite. Furthermore, the nanocomposite had a featureless X-ray pattern indicating a disordered-delaminated nanostructure. In this case the nanostructure shows more than a 140 °C higher decomposition temperature than the pure PDMS elastomer. In view of the improved barrier properties observed for other polymer nanocomposites (12), this increased thermal stability was attributed to hindered diffusion of volatile decomposition products within the nanocomposite. The TGA data for the aliphatic polyimide-clay nanocomposites also shows improved thermal stability. Additionally, Giannelis showed that the intercalated polyimide-clay nanocomposite is more stable than the delaminated nanocomposite; A somewhat surprising result since both samples contain the same mass fraction of clay (10 %) and the clay in the delaminated nanocomposite has a more homogenous

distribution. Self-extinguishing flammability behavior was reported while burning a 3 mm rod of the aliphatic polyimide-clay nanocomposites (12).

RESULTS

Flammability Properties. The Cone Calorimeter is one of the most effective bench-scale methods for studying the flammability properties of materials. The Cone Calorimeter measures fire-relevant properties such as heat release rate (HRR), and carbon monoxide yield, among others. Heat release rate, in particular peak HRR has been found to be the most important parameter to evaluate fire safety (19). We have characterized the flammability properties of a variety of polymer-clay nanocomposites, under fire-like conditions, using the Cone Calorimeter. We have observed reduced flammability for several thermoplastic polymer-clay nanocomposites; *delaminated* nylon-6 clay nanocomposites, and *intercalated* PS and PP clay nanocomposites (15). The cone calorimetry data (Table 1) shows that both the peak and average HRR were reduced significantly for *intercalated* and *delaminated* nanocomposites with low silicate mass fraction (2 % to 5 %). Similar results were also obtained for thermoset polymer nanocomposites made from vinyl esters and epoxies (15).

Table 1. Cone Calorimeter Data

Sample (structure)	Residue Yield (%) ± 0.5	Peak HRR (Δ%) (kW/m ²)	Mean HRR (Δ%) (kW/m ²)	Mean H _c (MJ/kg)	Mean SEA (m ² /kg)	Mean CO yield (kg/kg)
Nylon-6	1	1,010	603	27	197	0.01
Nylon-6 silicate- nanocomposite 2% <i>delaminated</i>	3	686 (32%)	390 (35%)	27	271	0.01
Nylon-6 silicate- nanocomposite 5% <i>delaminated</i>	6	378 (63%)	304 (50%)	27	296	0.02
PS	0	1,120	703	29	1,460	0.09
PS silicate- mix 3% <i>immiscible</i>	3	1,080	715	29	1,840	0.09
PS silicate- nanocomposite 3% <i>Intercalated/delaminated</i>	4	567 (48%)	444 (38%)	27	1,730	0.08
PS w/ DBDPO/Sb ₂ O ₃ 30%	3	491 (56%)	318 (54%)	11	2,580	0.14
PP	0	1,525	536	39	704	0.02
PP silicate nanocomposite 2% <i>intercalated</i>	5	450 (70%)	322 (40%)	44	1,028	0.02

Heat flux : 35 kW/m², H_c : Heat of combustion, SEA : Specific Extinction Area. Peak heat release rate, mass loss rate and specific extinction area (SEA) data, measured at 35 kW/m², are reproducible to within ± 10 %. The carbon monoxide and heat of combustion data are reproducible to within ± 15 %.

The heat release rate (HRR) plots for PP and PP clay-nanocomposites (mass fraction 2 % and 4 %) at 35 kW/m² heat flux are shown in Figure 3, and are typical of those found for all the nanocomposites in Table 1. The intercalated PP-clay (4 %) nanocomposite (layer spacing $d = 3.5$ nm) has a 75 % lower HRR than the pure PP. Comparison of the Cone Calorimeter data in Table 1, for the nylon-6, nylon-12, PS, and PP² nanocomposites, reveals that the heat of combustion (H_c), specific extinction area (SEA, a measure of smoke yield) and carbon monoxide yields are unchanged; this suggests that the source of the improved flammability properties of these materials is due to differences in condensed-phase decomposition processes, and not to a gas phase effect. For comparison, the flammability properties of PS flame retarded with decabromo diphenyloxide (DBDPO) and Sb₂O₃ are also shown in Table 1. These data show the primarily gas-phase effect of bromine. The resulting incomplete combustion is reflected in a lower heat of combustion and higher CO yield. The parameter primarily responsible for the lower HRR of the nanocomposites is the mass loss rate (MLR) during combustion. The MLR of the nanocomposite is significantly reduced from those values observed for the pure polymers (see Figure 4).

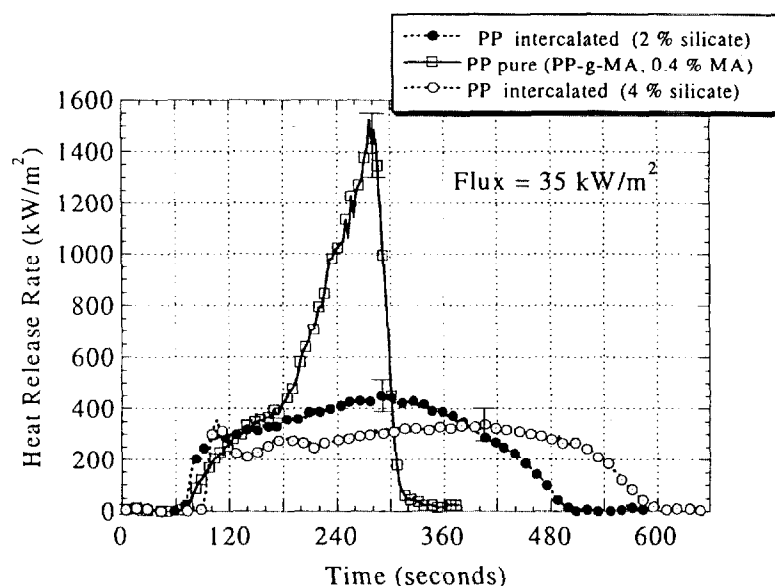


Figure 3. Comparison of the Heat Release Rate (HRR) plots for pure PPgMA, and two PPgMA-silicate (clay) nanocomposites, at 35 kW/m² heat flux, showing a 70 % to 80 % reduction in peak HRR for the nanocomposites with only a mass fraction of 2 % or 4 % clay, respectively.

Each of the thermoplastic nanocomposite systems we have examined shows essentially the same behavior when evaluated in the Cone Calorimeter. Furthermore, comparison of the residue yields (taken after combustion in the Cone Calorimeter) for the each of the nanocomposites in Table 1

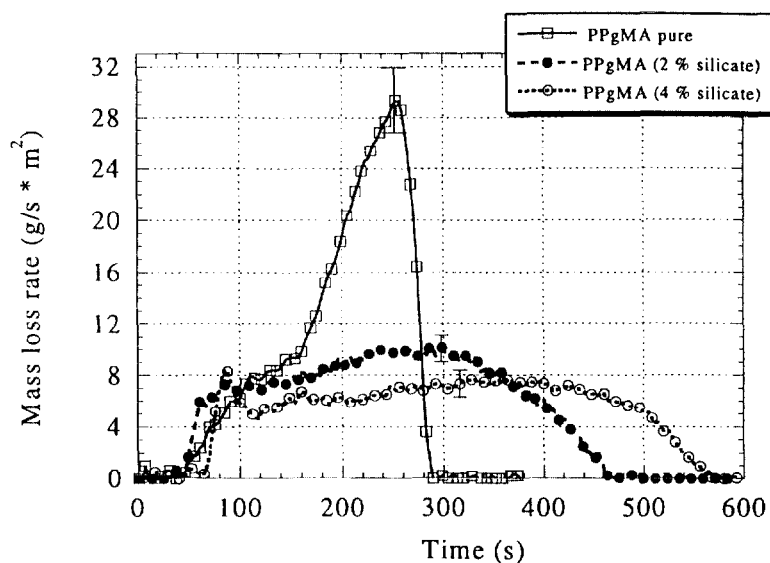


Figure 4. Mass loss rate plots for PPgMA, and two PPgMA-silicate (clay) nanocomposites.

reveals only a small improvement in the carbonaceous char yields, once the presence of the silicate in the residue is taken into account. These data indicate that the mechanism of flame retardancy may be very similar for each of the systems studied, and the lower flammability is not due to retention of a large fraction of fuel in the form of carbonaceous char in the condensed phase. Support for a common fire retardant mechanism comes from transmission electron microscopy (TEM) and x-ray diffraction (XRD) analysis of chars from a variety of nanocomposites. TEM images of sections of the combustion chars from nylon-6 silicate-nanocomposite (5 %) and cyanate ester-clay nanocomposite (6 %) are shown in Figure 5 and Figure 6, respectively. A multilayered carbonaceous-silicate structure is seen after combustion, with the darker, 1 nm thick, silicate sheets forming a large array of fairly even layers. The nanocomposite structure (intercalated and delaminated) appears to collapse during combustion. The nanocomposite structure present in the resulting char appears to enhance the performance of the char through reinforcement of the char layer, just as the nanostructure enhances the properties of the pure polymer. This multilayered carbonaceous-silicate structure may act as an excellent insulator and mass transport barrier, slowing the escape of the volatile products generated during decomposition (15). Analysis of combustion chars from nylon-6 and two epoxy nanocomposites, by XRD, shows that the interlayer spacing of all three chars is 1.3 nm (15). The cyanate ester-clay nanocomposite char has an interlayer spacing of 2.1 nm from TEM (Figure 6) and XRD possibly indicating that more carbonaceous char is captured between the silicate layers in this char than in the other nanocomposite chars (20). Presumably this is due to the inherent higher char yields (70 %) of cyanate esters as compared to nylon-6 (1 %) or epoxies (10 % to 15 %).

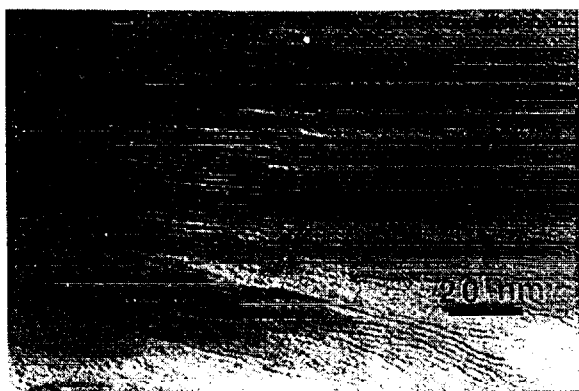


Figure 5. TEM of the combustion char from the nylon-6 silicate-nanocomposite (5 %) showing the carbon-silicate multilayered structure. Layer spacing = 1.3 nm.



Figure 6. TEM of the combustion char from the cyanate ester silicate-nanocomposite (6 %) showing the carbonaceous-silicate multilayered structure. Layer spacing = 2.1 nm.

Flammability of PS-layered silicate Nanocomposites. To attempt to understand how the structural properties of PS-nanocomposites influence flammability properties, we examined a range of nano-morphologies of PS-layered silicates. We looked at PS with a primary ammonium fluorohectorite (PS 3% C14-FH) and a PS with a quaternary ammonium MMT (PS 3 % 2C18-MMT). These two layered silicates disperse differently in PS. The TEM (Figure 8) of the PS 3% C14-FH shows it is an intercalated nanocomposite, while the TEM of PS 3 % 2C18-MMT shows it contains both intercalated MMT and delaminated MMT layers. Figure 7 shows that nearly 25 % of the MMT layers (1,2 to 3 layer stacks) are homogeneously dispersed in the PS matrix in PS 3 % 2C18-MMT. These PS nanocomposites also differ in that FH is a synthetic layered magnesium-silicate (unit cell formula: $Z_{1.6}^{+}[\text{Li}_{1.6}\text{Mg}_{4.4}(\text{Si}_{8.0})\text{O}_{20}\text{F}_4]$ where Z^{+} is the exchange cation) with a high aspect ratio (4 μm to 5 μm plate diameter), while MMT, an alumino-silicate (unit cell formula: $Z_{1.6}^{+}[\text{Mg}_{0.86}\text{Al}_{3.14}(\text{Si}_{8.0})\text{O}_{20}\text{OH}_4]$) has a lower aspect ratio (MMT plate diameter 0.1 μm to 1 μm).

Figure 9 shows the heat release rate data for the PS nanocomposites (MMT and FH) and two control samples: pure PS and PS mixed with sodium montmorillonite, which gives an immiscible, conventional, filled, composite. Surprisingly, the PS 3 % 2C18-MMT and PS 3% C14-FH behave very differently. The PS 3 % C14-FH has, within experimental uncertainty, no effect on the peak HRR, whereas the PS 3 % 2C18-MMT has a 60 % lower peak HRR as compared to the PS mixed with NaMMT. Since the two nanocomposites have different chemical formula of the layered silicate, different aspect ratios and different nano-morphologies, it is difficult to determine the exact reason for their very different flammability. However, in the aliphatic polyimide nanocomposite system, discussed above, both FH and MMT nanocomposites were found to have the same increase in thermal stability (by TGA) as long as they both were intercalated or both delaminated (13). The intercalated nanocomposite actually had better thermal stability than the delaminated nanocomposite. The possibility exists that only the delaminated PS nanocomposites have reduced flammability, however PP intercalated nanocomposites (with MMT) show excellent flammability properties. The lack of effectiveness for intercalated PS-FH

nanocomposite is in agreement with the Showa-Denko patent work on synthetic mica nylon-6 nanocomposites. The flammability of these nanocomposites was tested using the UL 94 test, and the results showed that more than 50 % of the FH had to be uniformly dispersed (delaminated) in stacks of 5 or fewer layers for a V-2 or V-0 rating to be obtained (16). Our view of the flame retardant mechanism is that a high performance carbonaceous-silicate char builds up on the nanocomposite's surface during burning, and that this insulates and slows the mass loss rate of decomposition products. This char layer forms as the polymer burns away and the silicate layers re-assemble into the multilayer char. We have shown reduced flammability for both delaminated and intercalated MMT nanocomposites. However, it appears only the delaminated FH nanocomposites are effective. Possibly, the large aspect ratio of the FH interferes with this re-assembly process. However, the potential difference in chemical reactivity of MMT versus FH can not be ruled out as a significant factor either.

Figure 10 shows the effect of processing conditions on the flammability of PS nanocomposites. When the PS 3 % 2C18-MMT nanocomposite is prepared via melt blending in an extruder (at 170 °C, under N₂ or vacuum) or by solvent (toluene) blending an intercalated/delaminated nanostructure results, which has reduced flammability. However, if the extrusion conditions include high temperatures and if air is not excluded the nanocomposite that forms has no improvement in flammability, as the data in Figure 10, for PS 3 % 2C18-MMT extruded at 185 °C, shows. This may be due to degradation during the extrusion (21).

SUMMARY

Polymer-clay nanocomposites are materials that in many of the cases studied have improved thermal properties. Furthermore, all MMT based nanocomposite systems reported so far also show improved flammability properties. The delaminated versions of nanocomposites also offer measurable improvements in a variety of physical properties. The intercalated versions also offer the above benefits, but with less improvement in physical properties. Many issues are unresolved as to the mechanism of these property enhancements. When they are resolved, nanocomposites may fulfill the requirements for a high performance additive-type flame retardant system; i.e., one that reduces flammability while improving the other performance properties of the final formulated product. This may be accomplished either as a single flame retardant additive or more likely in combination with other flame retardant additives (16).



Figure 7. TEM of PS (3 % 2C18-MMT). About 25 % of the MMT layers are delaminated with the remaining MMT intercalated with a layer spacing of 3.1 nm.

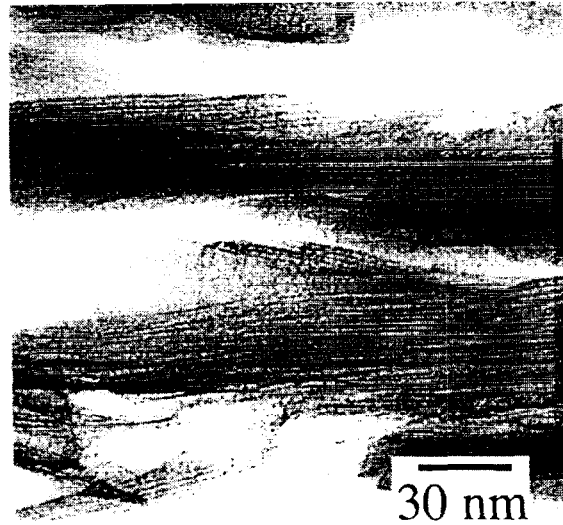


Figure 8. TEM of PS (3 % C14-FH) showing an intercalated nano-morphology with a layer spacing of 3.2 nm.

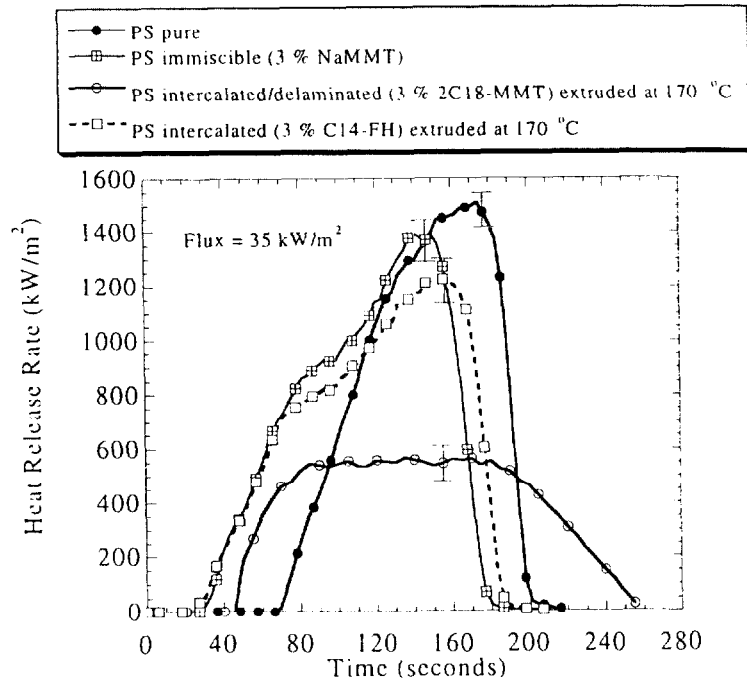


Figure 9. Heat Release Rate (HRR) plots for pure PS, PS w/NaMMT an immiscible-composite, PS w/ bis-C18 quaternary ammonium treated MMT and PS w/ C14 primary ammonium treated FH, at 35 kW/m² heat flux.

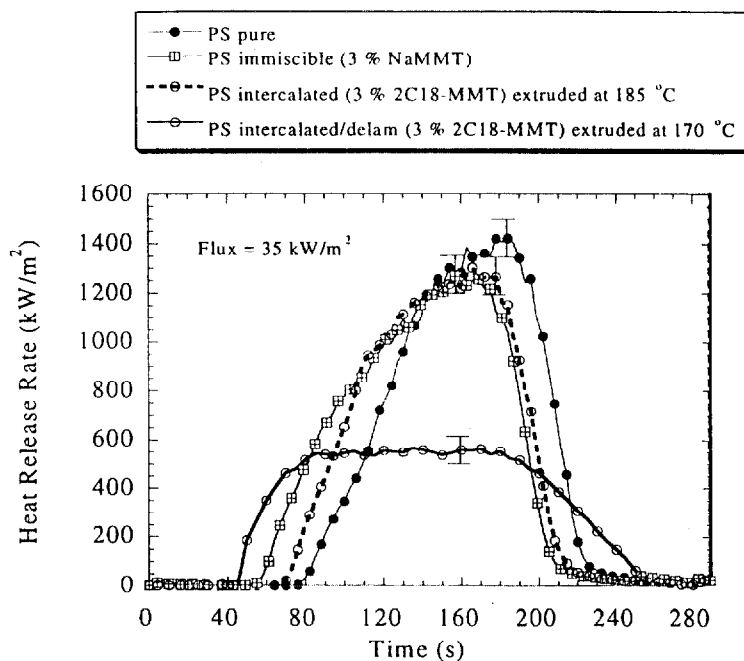


Figure 10. Heat Release Rate (HRR) plots for pure PS, PS w/NaMMT an immiscible-composite, PS w/ bis-C18 quaternary ammonium treated MMT and PS w/ bis-C18 quaternary ammonium treated MMT processed at 185 °C.

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³ Certain commercial equipment, instruments, materials, services or companies are identified in this paper in order to specify adequately the experimental procedure. This in no way implies endorsement or recommendation by NIST.

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